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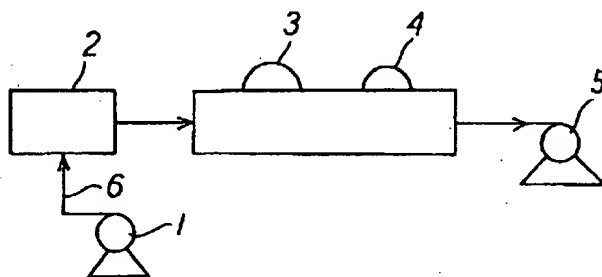
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(54) 【発明の名称】 食品包装材料における表面保護層の形成方法

(57) 【要約】

【課題】 狭い設置面積で高速処理を可能にする食品包装材料における表面保護層の形成方法を提供すること。

【解決手段】 巻出装置1から食品包装基材6をコーター2でその表面に電子線硬化型塗料を塗布し、電子線照射装置3で電子線を照射して塗料を硬化し、続いて紫外線照射装置4により紫外線を照射して電子線の照射による残留モノマーを処理する。これにより高速の硬化反応が可能な電子線を利用することができ、安全な食品包装材料の表面保護層を狭い設置面積で高速処理によって形成することができる。



【特許請求の範囲】

【請求項1】 食品包装材料に電子線硬化型塗料を塗布し、電子線照射にて前記塗料を硬化し、ついで紫外線照射にて残留モノマーを処理することを特徴とする食品包装材料における表面保護層の形成方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、電子線硬化型塗料を用いた食品包装材料における表面保護層の形成方法に関するものである。

【0002】

【従来の技術】食品包装材料は、基材表面に内容物の表示や絵柄等が印刷され、その上から透明な保護層が形成されている。この保護層は、印刷物の保護を図るだけでなく食品包装材料の光沢性、耐擦傷性、耐摩耗性等を高めるために形成されるもので、従来、この保護層の形成は、基材表面に熱硬化塗料を塗布し、加熱乾燥するいわゆる熱硬化方法で行われてきた。

【0003】

【発明が解決しようとする課題】しかし、熱硬化方法は、塗膜の硬化に長時間要し、また、大量生産を行うためには、長大な熱乾燥炉が必要であり高価な設備費、広い設置面積が必要なことなどの欠点がある。この欠点を解消する塗膜の硬化方法として、最近急速に伸展してきた紫外線硬化方法と電子線硬化方法を利用することが考えられる。

【0004】しかし、紫外線硬化方法は、安価な設備費、狭い設置面積で比較的高速処理が可能であるが、照射エネルギーが小さく光反応開始剤を添加して硬化する必要がある、硬化後の塗膜に光反応開始剤が残留し、その有毒性と場合により臭気発生等があるため、食品包装材料の塗膜としては重大な欠点となり、紫外線硬化方法をそのまま利用することはできない。

【0005】また、電子線硬化方法は、狭い設置面積で紫外線硬化方法より高速処理が可能であり、しかも光開始剤を添加して硬化する必要がないため理想的な硬化方法といえる。しかし、電子線硬化の場合は、極めて短い時間で硬化反応が進行するため、電子線の照射のバラツキ等によってわずかではあるが硬化物中にモノマーが取り残されることがある。この場合、食品衛生法の中の溶出試験方法で過マンガン酸カリウム消費量の項目に適合しないという欠点がある。

【0006】この残留モノマーを完全に消滅させるには、過大に電子線を照射させてやればよいが、この過大照射は不経済であるだけでなく、品質的にも過重合硬化塗膜が形成されて堅くなりすぎ、軽く折り曲げただけでもひび割れが生ずる等多数の問題が生じて好ましくなく、電子線硬化方法では適切な電子線の照射を図ることが困難であるという問題点がある。

【0007】本発明は、上記の問題点を鑑みなされたも

ので、狭い設置面積で高速処理を可能にする食品包装材料における表面保護層の形成方法を提供することを目的とする。

【0008】

【課題を解決するための手段】本発明の目的は、食品包装材料に電子線硬化型塗料を塗布し、電子線照射にて前記塗料を硬化し、ついで紫外線照射にて残留モノマーを処理することを特徴とする食品包装材料における表面保護層の形成方法とすることにより達成される。

【0009】本発明の上記特徴によれば、電子線照射直後には未反応のフリーラジカルが残っていて、この状態で紫外線を照射しているので、光開始剤を添加することなく電子線照射よりはるかに少ないエネルギーの紫外線で反応は促進され、硬化塗膜の物性をほとんど変化させることなく電子線照射後の残留モノマーのみを低減することができる。したがって、高速の硬化反応が可能な電子線および紫外線を利用することができ、安全な食品包装材料の表面保護層を狭い設置面積で高速処理によって形成することができる。

【0010】

【発明の実施の形態】以下、本発明に係る食品包装材料における表面保護層の形成方法の例について詳細に説明する。なお、図1ないし図3は本発明に係る表面保護層の形成方法に適用する装置構成図で、1は巻出装置、2はコーター、3は電子線照射装置、4は紫外線照射装置、5は巻取装置、6は食品包装基材をそれぞれ示している。

【0011】図1は電子線照射装置と紫外線照射装置が一体の構造にされ、その中を食品包装基材が連続的に搬送される状態を示し、図2は電子線照射装置と紫外線照射装置が別体に設置されていて、食品包装基材が電子線照射後一旦空気に触れて紫外線照射される状態を示し、図3は、電子線照射後一旦巻取られてから紫外線照射される状態を示している。

【0012】まず、原理について、紫外線硬化方法は、先にも述べたように照射エネルギーが小さいので、光反応開始剤を添加し、この光反応開始剤が紫外線からのエネルギーを受けて分解しラジカルが発生し、このラジカルが起点となって重合反応が進行していく。従って、光反応開始剤を添加しない状態では重合反応は開始されない。しかし、電子線照射直後には、未反応のフリーラジカルが残っているため、このフリーラジカルが残っている期間に紫外線照射を行うことによって光開始剤を添加することなくフリーラジカルが光反応の起点となる。この反応により残留モノマー同士が重合し、ポリマー化するので残留モノマーが低減できる。

【0013】電子線照射により発生するフリーラジカルの寿命は温度に依存し、温度が高くなる程短いという性質を有し、通常、室温にて1時間経過すると半減し、7時間経過すると大部分が消滅する。また、フリーラジカ

ルは酸素と反応しやすいので、多量の酸素雰囲気中に塗膜面が晒されると、表層部のフリーラジカルが減少するので残留モノマーとの反応が低減する。

【0014】一方、電子線照射処理装置は、塗膜硬化時の反応において塗料と酸素との反応及び電子線と酸素との衝突によってオゾンの発生などを防止するために、電子線照射は不活性ガスの窒素雰囲気下で行うようにされており、装置内は当然酸素が微量しか存在しない状態である。

【0015】したがって、最適には、図1に示すように、巻出装置1から食品包装基材6をコーター2でその表面に電子線硬化型塗料を塗布し、電子線照射装置3で電子線を照射して塗料を硬化し、続いて電子線照射装置3と一体化構造にされた紫外線照射装置4により紫外線を照射して電子線の照射による残留モノマーを処理し、処理後の食品包装基材6を巻取装置5に巻取る。

【0016】このようにすることにより、電子線照射後速やかに紫外線照射が行え、電子線照射後から紫外線照射が終了するまでフリーラジカルが酸素と反応する機会がなく、したがって、表層部の残留モノマーの反応が低減することなく最も効果的に残留モノマーが低減できる。

【0017】食品包装材料としての基材は、ポリ塩化ビニル、ポリエチレン、ポリプロピレン、ポリスチレン、ポリ塩化ビニリデン、ナイロン、ポリエチレンテレフレート等の単層またはこれらの複合シートもしくはチューブである。

【0018】電子線硬化型塗料は、官能基としてアクリロイル基を1個以上有するモノマーまたはオリゴマーであり、総称としてアクリル単量体と呼ぶ。

【0019】例えば、1官能のアクリル単量体としては、2-エチルヘキシルアクリレート、2-エチルヘキシルEO付加物アクリレート、2-フェノキシエチルアクリレート、フェノキシジエチレングリコールアクリレートなどである。

【0020】2官能のアクリル単量体としては、エチレングリコールジアクリレート、ポリエチレングリコールジアクリレート、トリプロピレングリコールジアクリレートなどである。

【0021】3官能以上有するアクリル単量体としては、トリメチロールプロパンテトラアクリレート、ジトリメチロールプロパンテトラアクリレート、ジペンタエリスリトールヘキサアクリレート、ジペンタエリスリトールカプロラクトン付加物ヘキサアクリレート、その他3官能以上のエステル系オリゴマー、ウレタン系オリゴマー、エポキシ系オリゴマーなどである。

【0022】電子線照射は、電子線の加速電圧は100～3000KV、線量は0.1～30Mradであり、好ましくは、加速電圧は150～300KV、線量は1～15Mradの範囲内である。照射雰囲気は、窒素の

ような不活性ガス雰囲気であり、残量酸素濃度は、500ppm以下が好ましい。

【0023】紫外線照射は、波長200～450nmの紫外線を発生する線源（一般に高圧水銀ランプ、メタルハライドランプなど）を有する装置であればよい。紫外線の照射量としては、30mJ/cm²以上であり、好ましくは50J/cm²以上である。

【0024】照射の間隔は、電子線照射後から紫外線照射までは、できるだけ素早く行うことが望ましく、また、その間塗膜面に空気が触れないようにすることが望ましいことから、図1に示す表面保護層の形成方法が最適であるが、図2に示すように、電子線照射直後に空気が触れても素早く紫外線照射を行なうか、あるいは図3に示すように、電子線照射直後に素早くフィルムの巻き取りを行えば、紫外線照射までの放置時間は空気が触れないので空気と反応するフリーラジカルの消滅は防止できる。

【0025】また、ラジカルは1日後でも僅かに存在するので紫外線照射量を多くすれば、光反応の起点が生じるが、この場合、大線量の紫外線を照射するため、不経済であること及び基材の材質によっては熱変形等が生じる恐れがある。

【0026】

【実施例】

実施例1、図1に示す装置構成にて、厚さ50μmのコロナ処理を施したポリエチレンフィルムを基材として用い、これに下記配合の混合組成物グラビアコートにて、塗布厚さ5μmとなるように塗布した。

①アクリロイルモルホン（ACMO興人（株）製）30重量部

②トリプロピレングリコールジアクリレート（アロニックスM-220東亜合成化学工業（株）製）40重量部

③ジペンタエリスリトールカプロラクトン付加物ヘキサアクリレート（カヤラッドDPCA-60日本化学（株）製）30重量部

【0027】塗布後、エリアビーム型電子線照射装置を用い、窒素雰囲気中、加速電圧150KV、線量10Mradの条件で行い塗膜を硬化し、直ちに紫外線照射装置にて10、30、50mJ/cm²の条件で照射を行った。この塗膜の食品衛生法の中の溶出試験方法で過マンガン酸カリウム消費量の結果は次の通りである。

10mJ/cm²で10.8ppm

30mJ/cm²で5.2ppm

50mJ/cm²で2.0ppm

【0028】実施例2、図2に示す装置構成にて、厚さ50μmのコロナ処理を施したポリエチレンフィルムを基材として用い、これに下記配合の混合組成物をグラビアコートにて、塗布厚さ5μmとなるように塗布した。

①アクリロイルモルホン（ACMO興人（株）製）30重量部

②トリプロピレングリコールジアクリレート（アロニックスM-220東亜合成化学工業（株）製）40重量部
 ③ジペンタエリストールカプロラクトン付加物ヘキサアクリレート（カヤラッドDPCA-60日本化学（株）製）30重量部

【0029】塗布後、エリアビーム型電子線照射装置を用い、窒素雰囲気中、加速電圧150KV、線量10Mradの条件で行い塗膜を硬化し、直ちに紫外線照射装置にて10、30、50mj/cm²の条件で照射を行った。この塗膜の食品衛生法の中の溶出試験方法で過マンガン酸カリウム消費量の結果は次の通りである。

10mj/cm²で13.5ppm

30mj/cm²で10.6ppm

50mj/cm²で3.7ppm

【0030】実施例3、図3に示す装置構成にて、厚さ50μmのコロナ処理を施したポリエチレンフィルムを基材として用い、これに下記配合の混合組成物グラビアコートにて、塗布厚さ5μmとなるように塗布した。

①アクリロイルモルホン（ACMO：興人（株）製）30重量部

②トリプロピレングリコールジアクリレート（アロニックスM-220東亜合成化学工業（株）製）40重量部

③ジペンタエリストールカプロラクトン付加物ヘキサアクリレート（カヤラッドDPCA-60日本化学（株）製）30重量部

【0031】塗布後、エリアビーム型電子線照射装置を用い、窒素雰囲気中、加速電圧150KV、線量10Mradの条件で行い塗膜を硬化した。5時間後に紫外線照射装置にて50、100、200mj/cm²の条件で照射を行った。この塗膜の食品衛生法の中の溶出試験方法で過マンガン酸カリウム消費量の結果は次の通りである。

50mj/cm²で13.4ppm

100mj/cm²で9.5ppm

200mj/cm²で6.3ppm

【0032】実施例4、図3に示す装置構成にて、厚さ50μmのコロナ処理を施したポリエチレンフィルムを基材として用い、これに下記配合の混合組成物グラビアコートにて、塗布厚さ5μmとなるように塗布した。

①アクリロイルモルホン（ACMO興人（株）製）30重量部

②トリプロピレングリコールジアクリレート（アロニックスM-220東亜合成化学工業（株）製）40重量部

③ジペンタエリストールカプロラクトン付加物ヘキサアクリレート（カヤラッドDPCA-60日本化学（株）製）30重量部

【0033】塗布後、エリアビーム型電子線照射装置を用い、窒素雰囲気中、加速電圧150KV、線量10Mradの条件で行い塗膜を硬化した。1日後に紫外線照射装置にて200、500、1000mj/cm²の条

件で照射を行った。この塗膜の食品衛生法の中の溶出試験方法で過マンガン酸カリウム消費量の結果は次の通りである。

200mj/cm²で29.4ppm 変形なし

500mj/cm²で17.3ppm 変形あり

1000mj/cm²で7.4ppm 変形あり

【0034】比較例1、電子線照射装置のみの装置構成にて、厚さ50μmのコロナ処理を施したポリエチレンフィルムを基材として用い、これに下記配合の混合組成物グラビアコートにて、塗布厚さ5μmとなるように塗布した。

①アクリロイルモルホン（ACMO興人（株）製）30重量部

②トリプロピレングリコールジアクリレート（アロニックスM-220東亜合成化学工業（株）製）40重量部

③ジペンタエリストールカプロラクトン付加物ヘキサアクリレート（カヤラッドDPCA-60日本化学（株）製）30重量部

【0035】塗布後、エリアビーム型電子線照射装置を用い、窒素雰囲気中、加速電圧150KV、線量10、30、50Mradの条件で行い塗膜を硬化した。この塗膜の食品衛生法の中の溶出試験方法で過マンガン酸カリウム消費量と塗膜の180度折り曲げ試験結果は次の通りである。

10Mradで38.2ppm 塗膜割れなし

30Mradで18.9ppm 塗膜割れなし

50Mradで8.7ppm 塗膜割れあり

【0036】食品衛生法の中の溶出試験方法で過カリウム消費量の項目では、その規格値は10ppm以下である。実施例1は空気に触れず電子線照射直後に照射する方法である。30mj/cm²で食品衛生法に合格する値が得られた。実施例2は電子線照射直後に紫外線照射を行っている。しかし、その間に空気に触れる条件であるため、50mj/cm²で食品衛生法に合格する値が得られた。

【0037】実施例3～4は電子線照射後紫外線照射までに5時間及び1日の保存時間があるが紫外線照射量が増加すると食品衛生法に合格する値が得られるが、照射量が多いとフィルムが変形するので多少問題がある。

【0038】比較例1は紫外線照射を行っていないので、30Mradまでは食品衛生法に不合格する値であるが、50Mradまで線量を増加すると合格する値になるが塗膜割れが生じて問題がある。

【0039】

【発明の効果】以上詳述したように、本発明によれば、食包装材料に電子線硬化型塗料を塗布し、電子線照射にて塗料を硬化後、未反応のフリーラジカルが残っている時間内で速やかに紫外線照射を行うことにより、硬化した塗膜からの残留モノマーの溶出を低減させることができ、食品衛生法の中の溶出試験方法で過マンガン酸カリ

ウム消費量の項目において合格させることができる。したがって、高速の硬化反応が可能な電子線を利用することができ、安全な食品包装材料の表面保護層を狭い設置面積で高速処理によって形成することができる。

【図面の簡単な説明】

【図1】本発明に係る表面保護層の形成方法に適用する一例の装置構成図である。

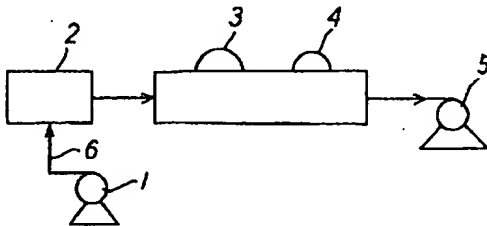
【図2】本発明に係る表面保護層の形成方法に適用する他の例の装置構成図である。

【図3】本発明に係る表面保護層の形成方法に適用する更に他の例の装置構成図である。

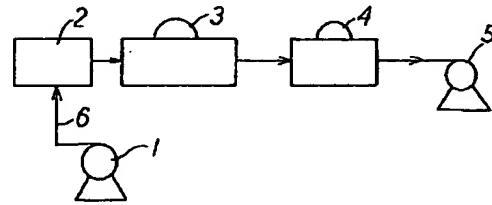
【符号の説明】

- 1 巻出装置
- 2 コーター
- 3 電子線照射装置
- 4 紫外線照射装置
- 5 巻取装置
- 6 食品包装基材

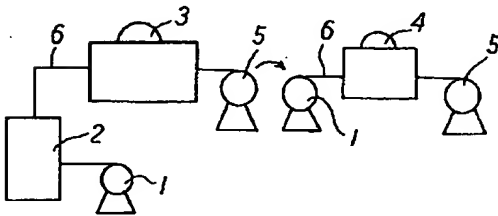
【図1】



【図2】



【図3】



Japanese Patent Application Laying Open (KOKAI) No. 9-302264
laid open on November 25, 1997

Japanese Patent Application No. 8-158759 (158759/96)
filed May 15, 1996

Priority: none

Applicant: NISSHIN HIGH VOLTAGE CO LTD, Japan

Title of the invention: Method for forming surface protective layer
of food packaging material

ABSTRACT

The presentation provides an overview of curable scratch resistant top coats for overprint protection on flexible and semirigid packaging materials to eliminate the need for an overprint film lamination. The top coat is cost effective while providing superior scratch resistance and reducing oxygen and moisture vapor transmission. The coating is applied by traditional printing or roll coating methods and is UV curable at reasonable production speeds. Future FDA acceptance for indirect food contact is under consideration.

Presented at Future-Pak 1997

October 28-29, 1997

METHOD FOR FORMING SURFACE PROTECTIVE LAYER OF FOOD PACKAGING MATERIAL

Patent Number: JP9302264
Publication date: 1997-11-25
Inventor(s): NAKAI KOJI
Applicant(s):: NISSIN HIGH VOLTAGE CO LTD
Requested Patent: ☐ JP9302264
Application Number: JP19960158759 19960515
Priority Number(s):
IPC Classification: C09D4/00 ; C08F2/48 ; C08F2/54 ; C08J7/04 ; C09D5/00
EC Classification:
Equivalents:

Abstract

PROBLEM TO BE SOLVED: To provide a method for forming a surface protective layer of a food packaging material in order to permit a high-speed treatment in a narrow installation area.
SOLUTION: The surface of a food packaging substrate material 6 unwound from an unwinding apparatus 1 is coated with an electron-beam-curable coating material, irradiated with an electron beam from an electron beam radiation apparatus 3 to cure the coating material, and irradiated with ultraviolet rays from an ultraviolet ray radiation apparatus 4 to treat the residual monomer after the electron beam irradiation. Thus, an electron beam capable of performing a high-speed curing can be utilized, enabling a safe surface protective layer of a food packaging material to be formed by a high-speed treatment in a narrow installation area.

translation pagination: page 1 of 10 pages

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(21) Application Number: Hei 8-158759 [158,759/1996]	(71) Applicant: 000226688 Nisshin High Voltage Co., Ltd. Ukyo-ku, Kyoto, Japan
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(74) Agent: Katsuhiro Kawasaki, Patent Attorney (and 1 other)	

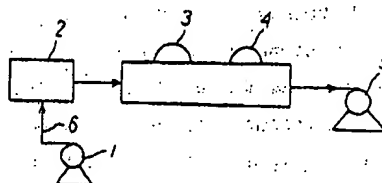
(54) Title of the Invention: Method for forming a surface-protective layer on food packaging materials

(57) Abstract

[Problem] To provide a method for forming a surface-protective layer on food packaging materials, wherein said method enables high-speed treatment in a small installation area.

[Solution] Using a coater 2, the surface of food packaging stock 6 from an unwinder 1 is coated with an electron beam-curable coating. This coating is first cured by exposure to an electron beam in electron beam irradiator 3 and is thereafter exposed to UV radiation in UV irradiator 4 in order to treat the residual monomer from electron beam exposure. This enables utilization of the electron beam — which is capable of high curing reaction rates — and makes possible the

formation of a safe surface-protective layer on the food packaging stock by high-speed treatment in a small installation area.



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Claim

[Claim 1] Method for forming a surface-protective layer on food packaging materials, said method being characterized by applying an electron beam-curable coating on a food packaging material, curing said coating by exposure to an electron beam, and treating the residual monomer by exposure to ultraviolet radiation.

Detailed Description of the Invention

[0001]

Field of the Invention

This invention relates to a method that uses an electron beam-curable coating to form a surface-protective layer on food packaging materials.

[0002]

Description of the Prior Art

During the utilization of food packaging materials, content descriptors and graphic elements are printed on the surface of the packaging stock and a transparent protective layer is then formed thereon. This protective layer is elaborated not only to protect the printed indicia, but also to enhance the gloss, scratch resistance, and wear resistance of the food packaging material. These protective layers have heretofore been formed by the so-called thermosetting method, in which a thermosetting

coating is applied on the stock surface and then dried by heating.

[0003]

Problems to Be Solved by the Invention

One problem with the thermosetting method is the long period of time required in order to cure the applied coating. This necessitates, in the case of mass production, a long and large drying oven, which in turn causes high equipment costs and requires a wide installation area. UV-curing and electron beam-curing technologies, which have recently undergone rapid development, have been contemplated as film curing technologies that would address these issues.

[0004]

UV-curing technology, while capable of relatively high-speed treatment in small installation areas at low equipment costs, nevertheless provides small irradiation energies and therefore requires that curing be carried out with the addition of a photoreaction initiator. This photoreaction initiator remains in the cured film, and its toxicity — and in some cases the evolution of an undesirable smell — are serious drawbacks to the use of the resulting coating for food packaging materials. These drawbacks prevent the use of UV-curing technology without some adaptation.

[0005]

Electron beam-curing technology is capable of even higher treatment speeds than UV-curing technology, and also uses a small installation area. Moreover, since this technology does not require the addition of a

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photoinitiator for curing, it could perhaps be considered as optimally qualified for application to food packaging materials. However, the curing reaction proceeds in a very short period of time in the case of electron beam curing, and monomer can remain in the cured product — although in very small amounts — as a consequence of nonuniformities in electron beam exposure. In such cases, the product cannot meet the potassium permanganate consumption requirement (elution test method) imposed by the Shokuhin-eisei-ho (the [Japanese] Food Sanitation Act)

[0006]

An excess electron beam exposure must be carried out in order to completely extinguish the residual monomer. This excess exposure is, however, not only uneconomical, but produces a cured film that is overpolymerized when considered from a quality standpoint. Such a film suffers from a number of problems: among others, it is hard and will crack when subjected to even gentle bending. It is therefore quite difficult to devise a suitable electron beam exposure level in the case of electron beam-curing technology.

[0007]

This invention was developed in view of the problems described above, and takes as its object the introduction of a method for forming a surface-protective layer on food packaging materials that enables high-speed treatment in a small installation area.

[0008]

Means Solving the Problems

The object of the invention is achieved by a method for forming a surface-protective layer on food packaging materials, said method being characterized by applying an electron beam-curable coating on a food packaging material, curing said coating by exposure to an electron beam, and treating the residual monomer by exposure to ultraviolet radiation.

[0009]

According to the characteristic features of this invention, since exposure to UV radiation is carried out in the presence of the unreacted free radicals that remain immediately after electron beam exposure, reaction can be promoted by the UV radiation — which is much less energetic than the irradiated electron beam — in the absence of a photoinitiator. This achieves a reduction only in the residual monomer from electron beam exposure with almost no change in the physical properties of the cured film. Thus, the electron beam and UV radiation, which are both capable of high curing reaction rates, can be used in combination to enable the high-speed production in a small installation area of a safe surface-protective layer on food packaging materials.

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[0010]

Embodiments of the invention

Examples of the inventive method for forming a surface-protective layer on food packaging materials will be explained in detail in the following. Figures 1 through 3 contain structural diagrams of apparatuses usable by the inventive method for forming a surface-protective film. In Figures 1 through 3, 1 refers to an unwinder, 2 refers to a coater, 3 refers to an electron beam irradiator, 4 refers to an ultraviolet irradiator, 5 refers to a take-up apparatus, and 6 refers to the food packaging stock.

[0011]

Figure 1 depicts a configuration in which the electron beam irradiator and UV irradiator area are combined into a single unit and the food packaging stock is continuously transported through this unit. Figure 2 depicts a configuration in which the electron beam irradiator and UV irradiator are set up as separate structures and the food packaging stock is brought into temporary contact with the air after electron beam exposure and is thereafter subjected to UV irradiation. Figure 3 shows a configuration in which the stock is temporarily wound up after electron beam exposure and is thereafter subjected to UV irradiation.

[0012]

The principles underlying this invention will be considered first. UV-curing technology requires the addition of a photoreaction initiator due, as mentioned above, to this technology's

low level of irradiated energy. This photoreaction initiator undergoes decomposition upon absorption of energy from the UV radiation with the production of radicals. These radicals act as initiation points and the polymerization reaction proceeds therefrom. Thus, polymerization reactions are not initiated when the photoreaction initiator is not present. However, unreacted free radicals remain immediately after electron beam exposure. The execution of UV irradiation in the time interval during which these free radicals remain enables the free radicals to assume the role of initiation points for the photoreaction in the absence of a photoinitiator. This reaction results in polymerization of residual monomer with itself with ensuing decline in the amount of residual monomer as the monomer is converted into polymer

[0013]

The lifetime of the free radicals produced by electron beam irradiation depends on the temperature: higher temperatures result in shorter lifetimes. Typically the population is depleted by half after 1 hour at room temperature, and a major fraction is extinguished after 7 hours. In addition, since free radicals readily react with oxygen, exposure of the film surface to an oxygen-rich atmosphere also results in depletion of the free radicals in the surface region and hence in a reduction in the reaction with residual monomer.

[0014]

However, electron beam irradiators are designed to implement electron beam irradiation under a nitrogen (inert gas) atmosphere in order during the film cure operation to prevent ozone

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generation by reaction between the film and oxygen and collisions between the electron beam and oxygen. The interior of the irradiator therefore resides under a very oxygen-poor state. [0015]

Therefore, in the optimal configuration, the surface of food packaging stock 6 from the unwinder 1 is coated by the coater 2 with an electron beam-curable coating; this coating is cured by exposure to an electron beam in the electron beam irradiator 3; the residual monomer from electron beam exposure is then treated by exposure to UV radiation in a UV irradiator 4 that is integrated into a single unit with the electron beam irradiator 3; and the treated food packaging stock 6 is wound up on the take-up apparatus 5. [0016]

In this configuration, exposure to UV radiation is carried out immediately after electron beam exposure, and the free radicals therefore have no opportunity to react with oxygen during the interval from completion of electron beam exposure to completion of UV exposure. This affords the most effective depletion of residual monomer since the reaction of residual monomer in the surface region is not inhibited. [0017]

The stock making up the food packaging material can be a monolayer or composite sheet or tube of, for example, polyvinyl chloride, polyethylene, polypropylene, polystyrene, polyvinylidene chloride, nylon, or polyethylene terephthalate. [0018]

The electron beam-curable coating can be, for example, monomer or oligomer containing at least 1 acryloyl group as its functional group; these are generally known as acrylic monomer. [0019]

Monofunctional acrylic monomer can be exemplified by 2-ethylhexyl acrylate, 2-ethylhexyl-EO adduct acrylate, 2-phenoxyethyl acrylate, and phenoxydiethylene glycol acrylate. [0020]

Difunctional acrylic monomer can be exemplified by ethylene glycol diacrylate, polyethylene glycol diacrylate, and tripropylene glycol diacrylate. [0021]

Trifunctional and higher functional acrylate monomer can be exemplified by trimethylolpropane triacrylate, ditrimethylolpropane tetraacrylate, dipentaerythritol hexaacrylate, dipentaerythritol-caprolactone adduct hexaacrylate, and trifunctional and higher functional oligoesters, urethane-type oligomers, and epoxy-type oligomers. [0022]

With regard to electron beam irradiation, the electron beam acceleration voltage should be from 100 to 3,000 kV and the dose should be from 0.1 to 30 Mrad, while the acceleration voltage is preferably from 150 to 300 kV and the dose is preferably from 1 to 15 Mrad. The irradiation atmosphere should be an inert gas atmosphere, such as nitrogen, in which the residual oxygen concentration is preferably no more than 500 ppm.

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[0023]

UV irradiation can be carried out from an apparatus that has a source (typically a high-pressure mercury lamp or metal halide lamp) that produces UV radiation with a wavelength from 200 to 450 nm. The UV dose should be at least 30 mJ/cm² and is preferably at least 50 mJ/cm².

[0024]

The gap between electron beam exposure and UV exposure is preferably traversed as rapidly as possible, and during this traverse the film surface preferably does not come into contact with air. Given these preferred features, the method shown in Figure 1 for forming the surface-protective film is optimal. However, as shown in Figure 2, in another possible embodiment UV exposure can be carried out immediately after electron beam exposure even with contact between the air and film surface. In yet another possible embodiment as shown in Figure 3, the film can be rapidly wound up immediately after electron beam exposure and held prior to UV exposure out of contact with air in order to prevent extinction of the free radicals by reaction with the air.

[0025]

Since radicals will be present — although in very small amounts — even after 1 day, initiation points for the photoreaction can be produced at this time as long as a large UV exposure dose is used. However, the use of large UV doses in such cases is uneconomical and also runs the risk of producing thermal deformation in the substrate depending on the particular type of substrate.

[0026]

Examples

Example 1

This example used the apparatus whose structure is shown in Figure 1. The stock in this case was 50 µm-thick polyethylene film that had been subjected to a corona treatment. The following mixed composition was coated thereon using a gravure coater so as to produce a coating thickness of 5 µm:

- (1) 30 weight parts acryloylmorpholine (ACMO from Kojin KK),
- (2) 40 weight parts tripropylene glycol diacrylate (Aronix M-220 from Toa Gosei Kagaku Kogyo KK), and
- (3) 30 weight parts dipentaerythritol-caprolactone adduct hexaacrylate (Kayarad DPCA-60 from Nippon Kagaku KK).

[0027]

After the coating operation, the film was cured using an area beam-type electron beam irradiator. This curing was run in a nitrogen atmosphere using an acceleration voltage of 150 kV and a dose of 10 Mrad. Curing was followed immediately by exposure in the UV irradiator at 10, 30, or 50 mJ/cm². The resulting films were tested for their potassium permanganate consumption using the elution testing methodology in the Food Sanitation Act, and the following values were obtained.

10.8 ppm at 10 mJ/cm²5.2 ppm at 30 mJ/cm²2.0 ppm at 50 mJ/cm²

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[0028]

Example 2

This example used the apparatus whose structure is shown in Figure 2. The stock in this case was 50 μm -thick polyethylene film that had been subjected to a corona treatment. The following mixed composition was coated thereon using a gravure coater so as to produce a coating thickness of 5 μm :

- (1) 30 weight parts acryloylmorpholine (ACMO from Kojin KK),
- (2) 40 weight parts tripropylene glycol diacrylate (Aronix M-220 from Toa Gosei Kagaku Kogyo KK), and
- (3) 30 weight parts dipentaerythritol-caprolactone adduct hexaacrylate (Kayarad DPCA-60 from Nippon Kagaku KK).

[0029]

After the coating operation, the film was cured using an area beam-type electron beam irradiator. This curing was run in a nitrogen atmosphere using an acceleration voltage of 150 kV and a dose of 10 Mrad. Curing was followed immediately by exposure in the UV irradiator at 10, 30, or 50 mJ/cm^2 . The resulting films were tested for their potassium permanganate consumption using the elution testing methodology in the Food Sanitation Act, and the following values were obtained.

13.5 ppm at 10 mJ/cm^2 10.6 ppm at 30 mJ/cm^2 3.7 ppm at 50 mJ/cm^2

[0030]

Example 3

This example used the apparatus whose structure is shown in Figure 3. The stock in this case was 50 μm -thick polyethylene film that had been subjected to a corona treatment. The following mixed composition was coated thereon using a gravure coater so as to produce a coating thickness of 5 μm :

- (1) 30 weight parts acryloylmorpholine (ACMO from Kojin KK),
- (2) 40 weight parts tripropylene glycol diacrylate (Aronix M-220 from Toa Gosei Kagaku Kogyo KK), and
- (3) 30 weight parts dipentaerythritol-caprolactone adduct hexaacrylate (Kayarad DPCA-60 from Nippon Kagaku KK).

[0031]

After the coating operation, the film was cured using an area beam-type electron beam irradiator. This curing was run in a nitrogen atmosphere using an acceleration voltage of 150 kV and a dose of 10 Mrad. After holding for 5 hours, exposure in the UV irradiator was then run at 50, 100, or 200 mJ/cm^2 . The resulting films were tested for their potassium permanganate consumption using the elution testing methodology in the Food Sanitation Act, and the following values were obtained.

13.4 ppm at 50 mJ/cm^2 9.5 ppm at 100 mJ/cm^2 6.3 ppm at 200 mJ/cm^2

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[0032]

Example 4

This example used the apparatus whose structure is shown in Figure 3. The stock in this case was 50 μm -thick polyethylene film that had been subjected to a corona treatment. The following mixed composition was coated thereon using a gravure coater so as to produce a coating thickness of 5 μm :

- (1) 30 weight parts acryloylmorpholine (ACMO from Kojin KK),
- (2) 40 weight parts tripropylene glycol diacrylate (Aronix M-220 from Toa Gosei Kagaku Kogyo KK), and
- (3) 30 weight parts dipentaerythritol-caprolactone adduct hexaacrylate (Kayarad DPCA-60 from Nippon Kagaku KK).

[0033]

After the coating operation, the film was cured using an area beam-type electron beam irradiator. This curing was run in a nitrogen atmosphere using an acceleration voltage of 150 kV and a dose of 10 Mrad. After holding for 1 day, exposure in the UV irradiator was then run at 200, 500, or 1,000 mJ/cm^2 . The resulting films were tested for their potassium permanganate consumption using the elution testing methodology in the Food Sanitation Act, and the following values were obtained.

- 29.4 ppm at 200 mJ/cm^2 , no deformation
- 17.3 ppm at 500 mJ/cm^2 , deformation occurred
- 7.4 ppm at 1,000 mJ/cm^2 , deformation occurred

[0034]

Comparative Example 1

This example used an apparatus composed of only an electron beam irradiator. The stock in this case was 50 μm -thick polyethylene film that had been subjected to a corona treatment. The following mixed composition was coated thereon using a gravure coater so as to produce a coating thickness of 5 μm :

- (1) 30 weight parts acryloylmorpholine (ACMO from Kojin KK),
- (2) 40 weight parts tripropylene glycol diacrylate (Aronix M-220 from Toa Gosei Kagaku Kogyo KK), and
- (3) 30 weight parts dipentaerythritol-caprolactone adduct hexaacrylate (Kayarad DPCA-60 from Nippon Kagaku KK).

[0035]

After the coating operation, the film was cured using an area beam-type electron beam irradiator. This curing was run in a nitrogen atmosphere using an acceleration voltage of 150 kV and a dose of 10, 30, or 50 Mrad. The resulting films were tested for their potassium permanganate consumption using the elution testing methodology in the Food Sanitation Act, and the obtained values are reported below. Also reported below are the results from 180° bending tests executed on the films.

- 38.2 ppm at 10 Mrad, no film cracking
- 18.9 ppm at 30 Mrad, no film cracking
- 8.7 ppm at 50 Mrad, film cracking occurred

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[0036]

The Food Sanitation Act specifies a value of ≤ 10 ppm for the potassium permanganate consumption measured using the Act's elution testing methodology. Example 1, which involved UV irradiation immediately after electron beam exposure, gave a value that satisfied the Food Sanitation Act at 30 mJ/cm^2 . Example 2 also involved UV irradiation immediately after electron beam exposure, but with contact with the air between the two treatments. In this case, 50 mJ/cm^2 was required to give a value that satisfied the Food Sanitation Act.

[0037]

Examples 3 and 4 employed a holding period of 5 hours and 1 day, respectively, between electron beam exposure and UV exposure. Values meeting the Food Sanitation Act were obtained when the UV dose was increased, but the higher doses were somewhat problematic because they caused film deformation to occur.

[0038]

Comparative Example 1 did not use UV irradiation, and as a result the values did not comply with the Food Sanitation Act up to and including 30 Mrad. Although a compliant value was obtained when the dose was raised up to 50 Mrad, film cracking was produced at this dose level.

[0039]

Advantageous Effects of the Invention

As has been described above, this invention can decrease elution of residual monomer from the cured film. The invention

achieves this as follows: after application of an electron beam-curable coating on food packaging material and cure of this coating by exposure to an electron beam, exposure to UV radiation is immediately carried out within the time interval in which unreacted free radicals still remain in situ. The decreased residual monomer elution enables compliance with the potassium permanganate consumption by elution testing that is stipulated in the Food Sanitation Act. This enables utilization of electron beam technology, with its capacity for high curing reaction rates, and enables the formation of a safe surface-protective layer on food packaging materials at high treatment speeds and in small installation spaces.

Brief Description of the Drawings

Figure 1 contains a structural drawing of one example of an apparatus that can be used by the method according to the present invention for forming surface-protective layers.

Figure 2 contains a structural drawing of another example of an apparatus that can be used by the method according to the present invention for forming surface-protective layers.

Figure 3 contains a structural drawing of yet another example of an apparatus that can be used by the method according to the present invention for forming surface-protective layers.

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[Reference Symbols]

- 1 ----- unwinder
- 2 ----- coater
- 3 ----- electron beam irradiator
- 4 ----- UV irradiator
- 5 ----- take-up apparatus
- 6 ----- food packaging stock

Figure 1.

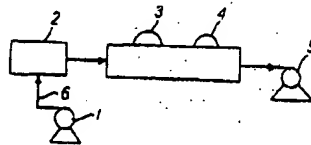


Figure 2.

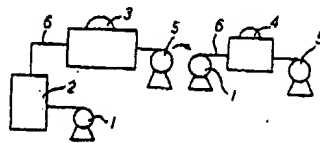
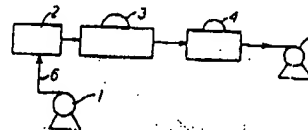


Figure 3.